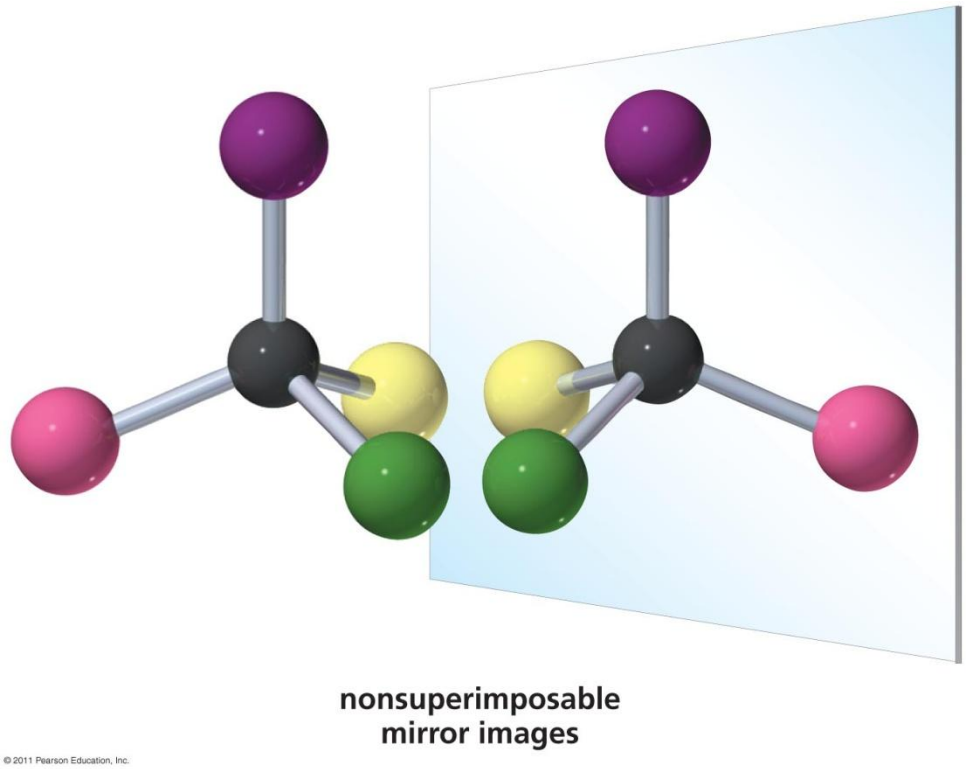
Organic Chemistry
2th Edition
Paula Yurkanis Bruice



nonsuperimposable mirror images

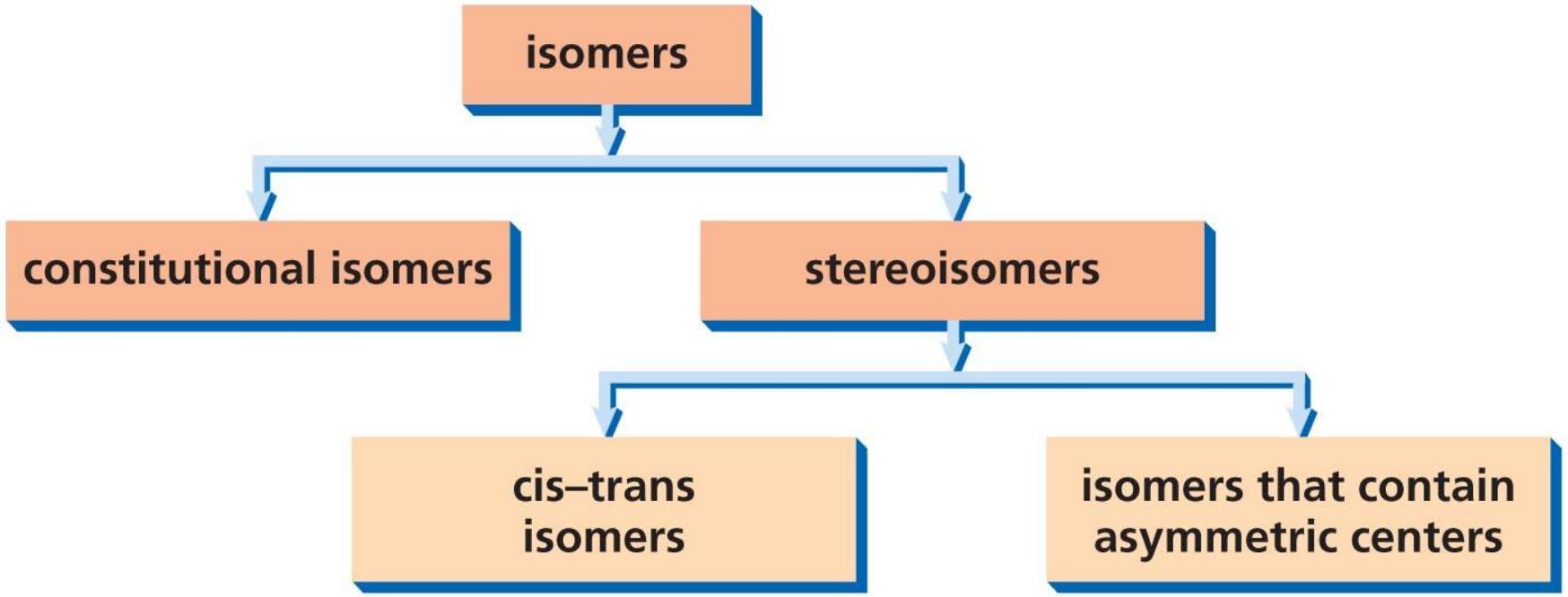
Chapter 6

Stereochemistry

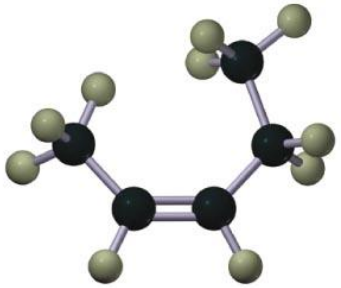
The Arrangement of Atoms in Space; The Stereochemistry of Addition Reactions

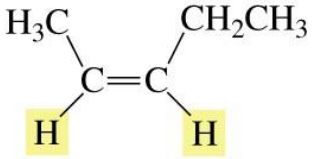
Isomers

Non-identical compounds having the same molecular formula

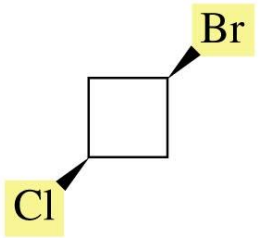


Cis-Trans Isomers in Alkenes and Rings

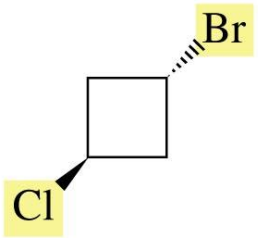




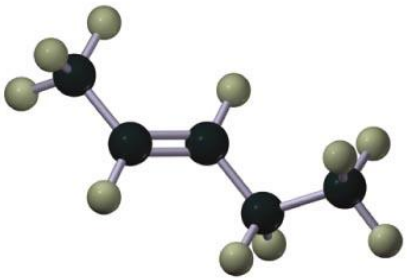
cis-2-pentene

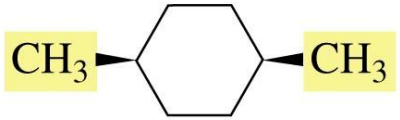


cis-1-bromo-3-chlorocyclobutane

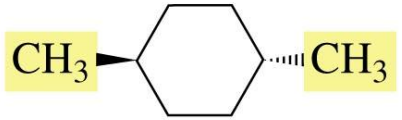


trans-1-bromo-3-chlorocyclobutane

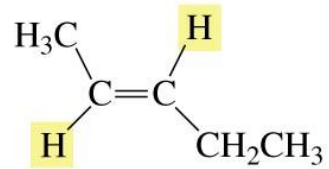




cis-1,4-dimethylcyclohexane



trans-1,4-dimethylcyclohexane

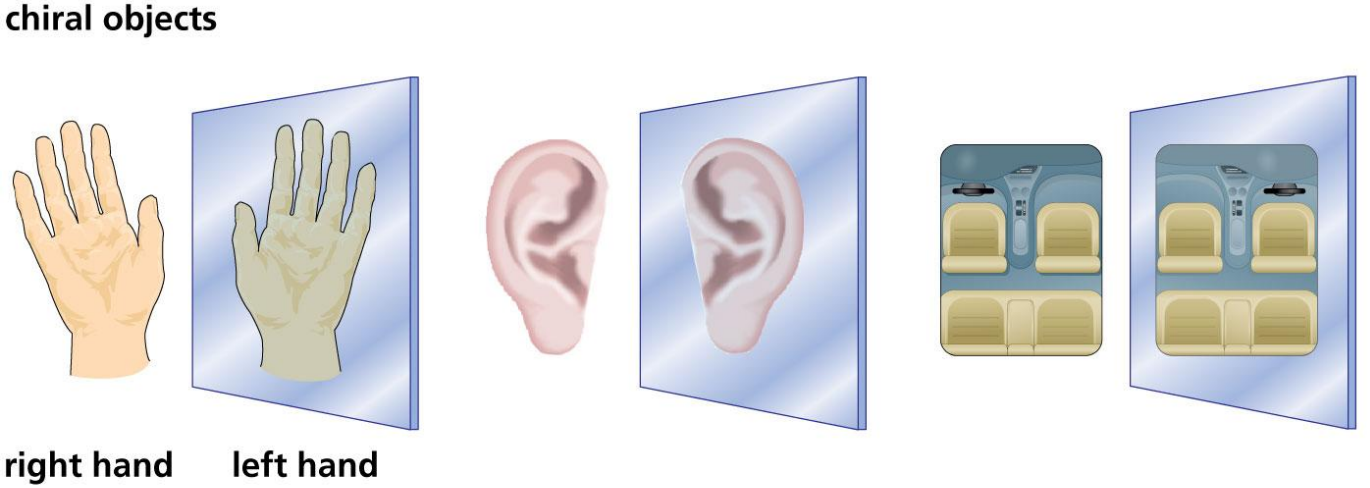


trans-2-pentene

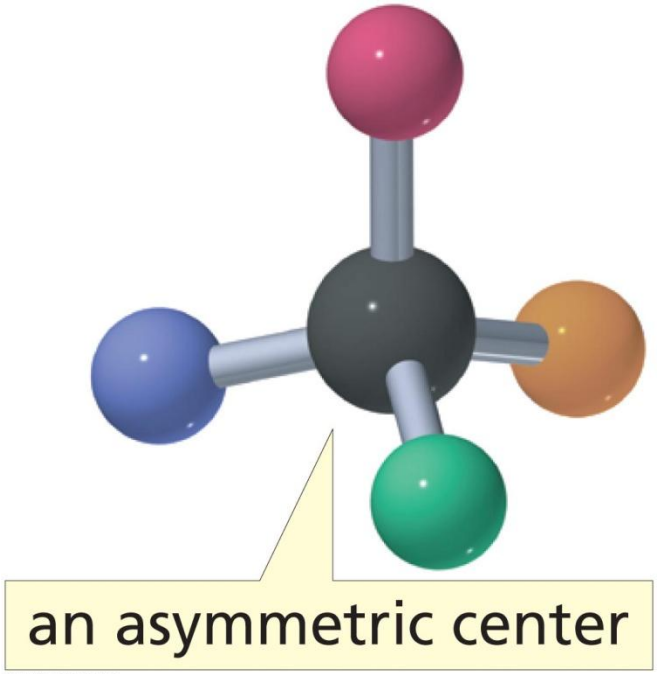
Stereoisomerism

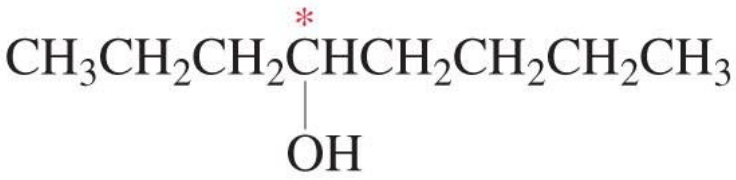
- Another kind of configurational isomerism.
- ***Chiral*** – Nonsuperimposable on its mirror image.
- ***Achiral*** – Superimposable on its mirror image.
- If a molecule (or object) has a mirror plane or an inversion center, it cannot be chiral.

Common Objects Also Exhibit Chirality or Achirality

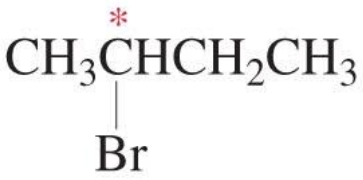


An Asymmetric Center Is a Cause of Chirality

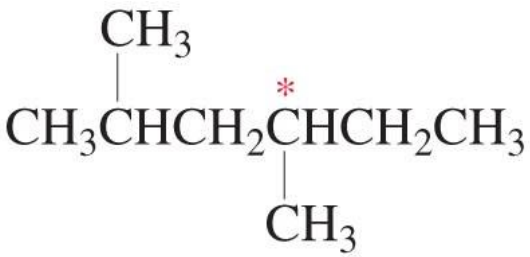




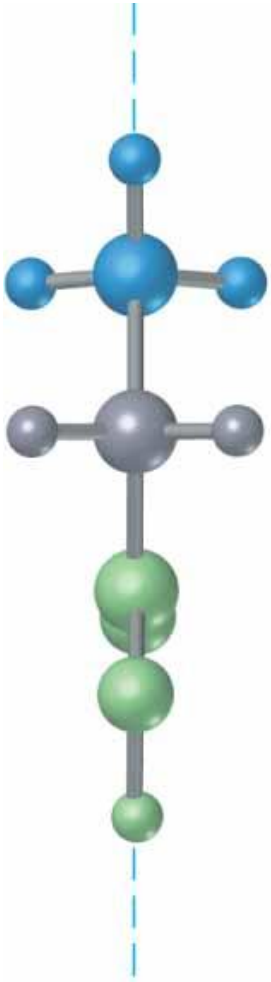
4-octanol



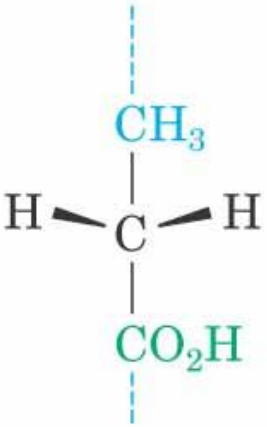
2-bromobutane



2,4-dimethylhexane



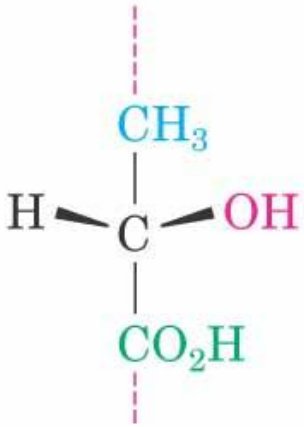
Symmetry plane



$CH_3CH_2CO_2H$

Propanoic acid (achiral)

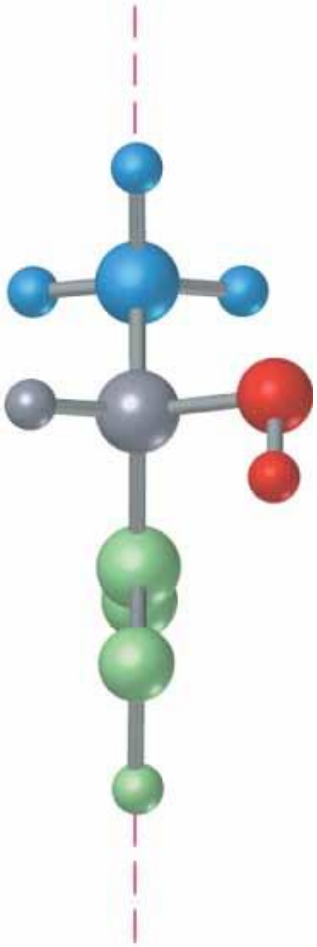
NOT symmetry plane



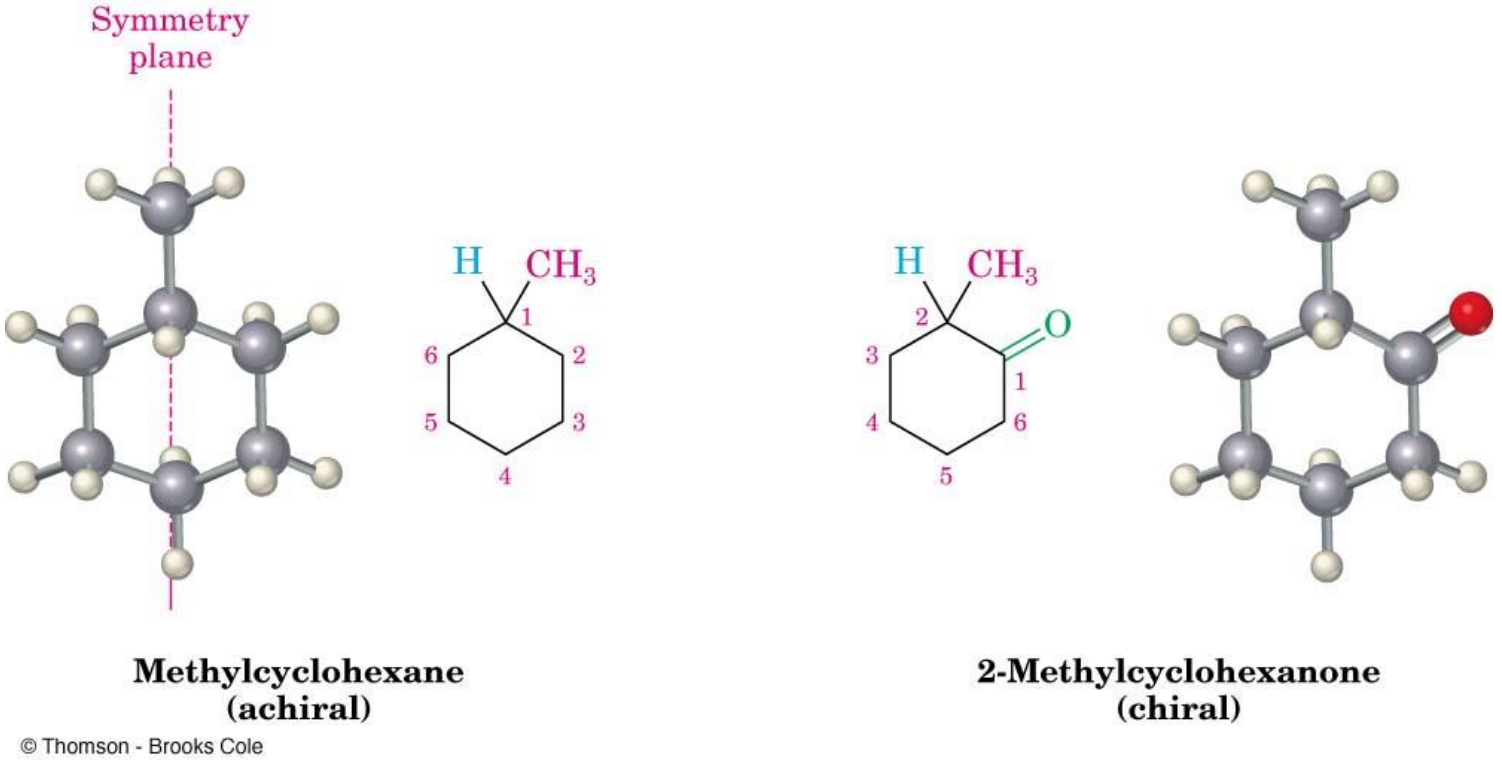
OH

CH_3CHCO_2H

Lactic acid (chiral)



- Groups are considered “different” if there is any structural variation (if the groups could not be superimposed if detached, they are different)
- In cyclic molecules, we compare by following in each direction in a ring



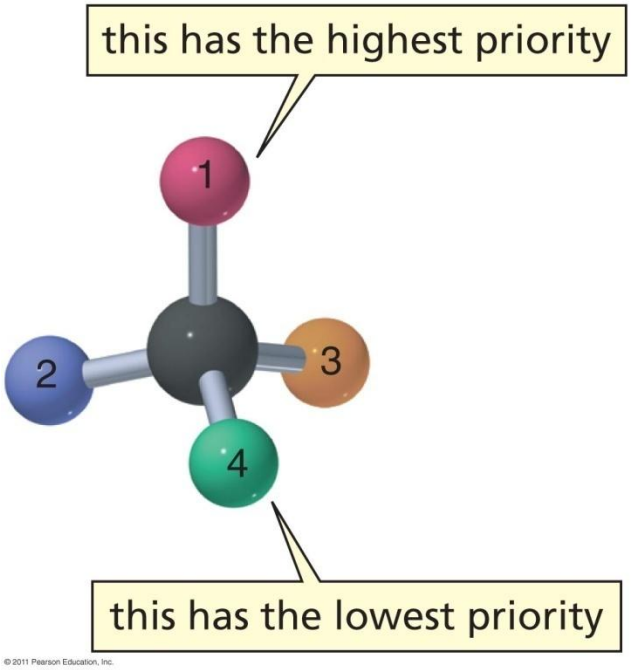
Methylcyclohexane (achiral)

2-Methylcyclohexanone (chiral)

Naming Enantiomers

The *R,S* system of nomenclature

Rank the groups (atoms) bonded to the asymmetric center.



Ranking Rules:

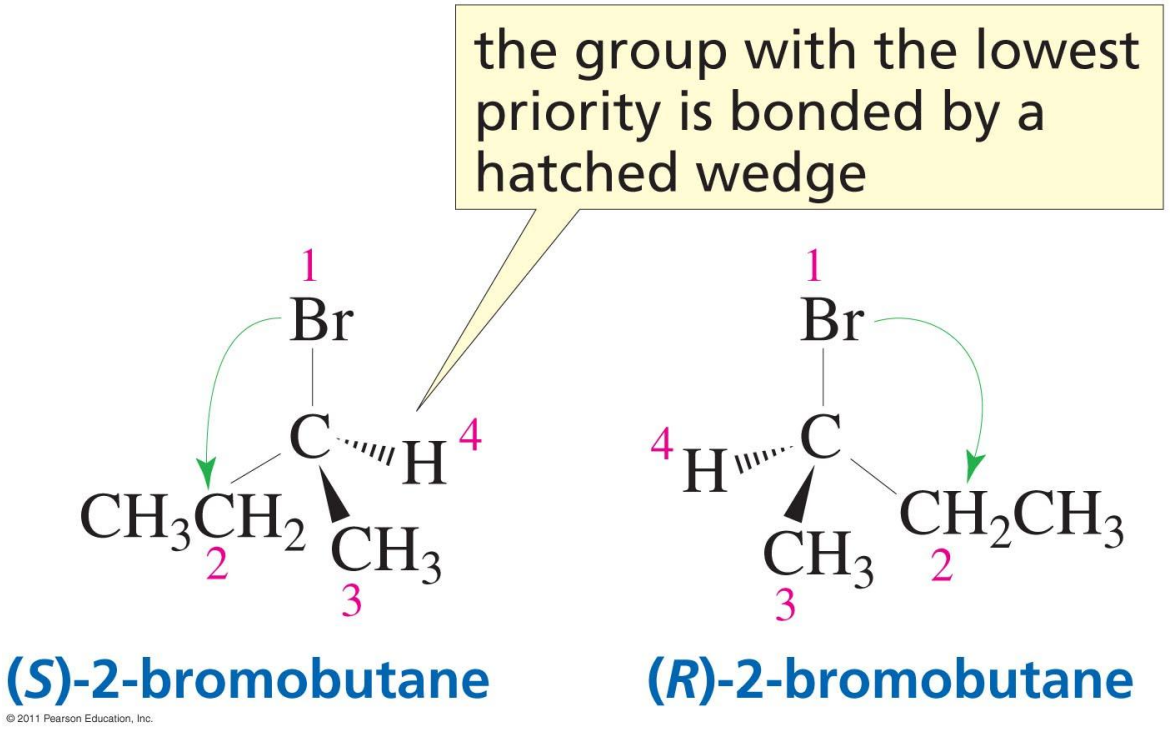
1. **Consider the atomic number of the atoms bonded directly to the asymmetric carbon.**
2. **If there is a tie, consider the atoms attached to the tied atoms.**
3. **Multiple bonds are treated as attachment of multiple single bonds using "divide-duplicate."**
4. **Rank the priorities by mass number in isotopes.**

Same rules as for *E*/*Z* assignments

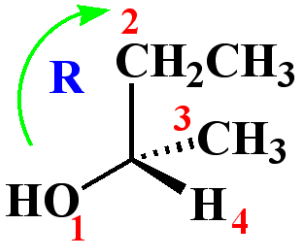
- **Clockwise = *R* configuration**
- **Counterclockwise = *S* configuration**

Naming from the Perspective Formula

1. **Rank the groups bonded to the asymmetric center with the lowest priority group in the back.**

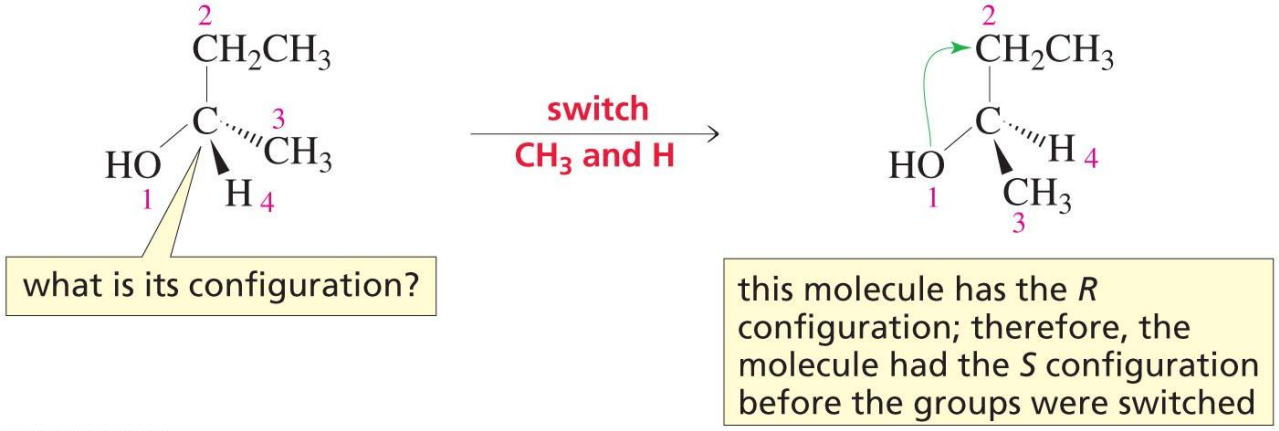


2. If the group (or atom) with the lowest priority is in the front, assign S or R and then switch your answer to R or S respectively.



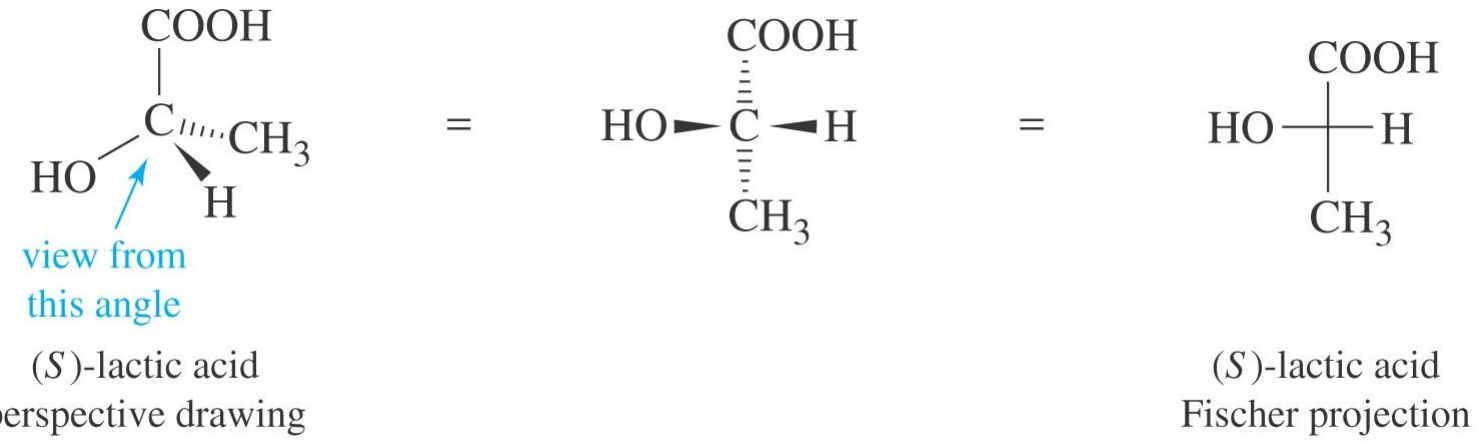
Configuration is S

3. Alternatively, atoms or groups can be switched so as to place the lowest priority group in the back. One switch: configuration opposite; two switches, configuration unchanged.



Fischer Projection Formulas

- Flat drawing that represents a 3D molecule.
- A chiral carbon is at the intersection of horizontal and vertical lines.
- Horizontal lines are forward, out-of-plane.
- Vertical lines are behind the plane.

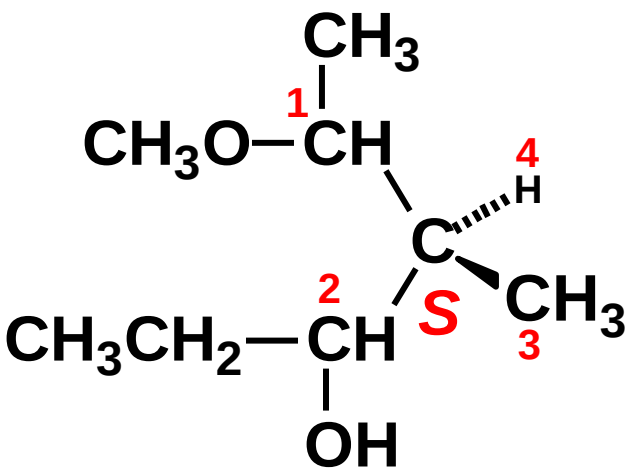


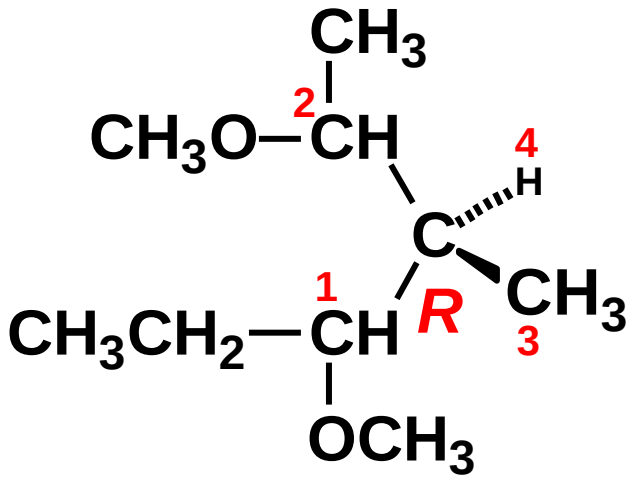
(*S*)-lactic acid
perspective drawing

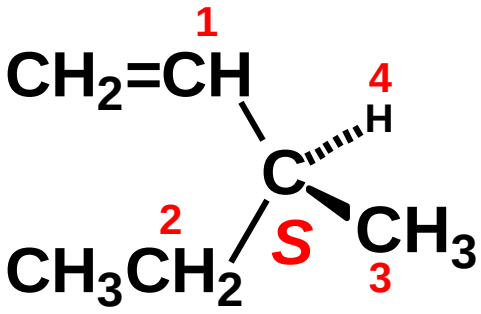
(*S*)-lactic acid
Fischer projection

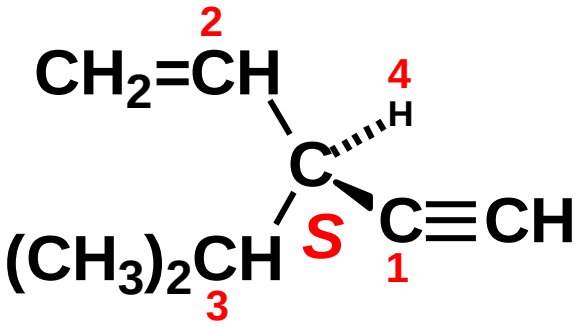
Absolute Configuration

- **Determine the absolute configuration of the following compounds:**









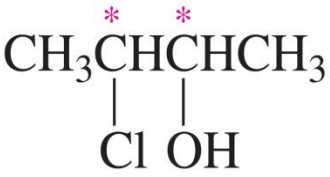
Racemic Mixtures

- Equal quantities of *d*- and *l*-enantiomers.
- Notation: (*d,l*) or (±)
- No optical activity.
- The mixture may have different b.p. and m.p. from the enantiomers!

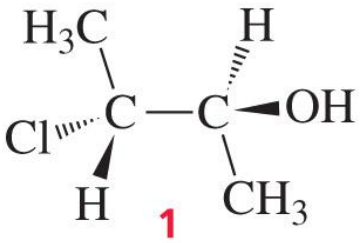
=>

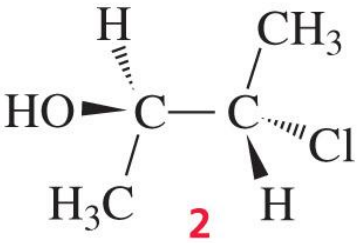
Compounds with More Than One Stereogenic Center:

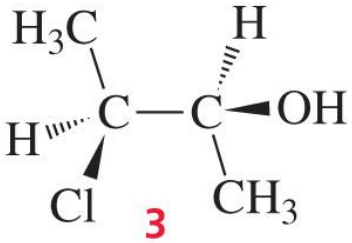
a maximum of 2^n stereoisomers can be obtained

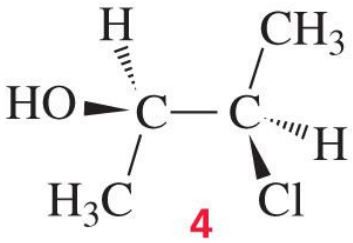


3-chloro-2-butanol



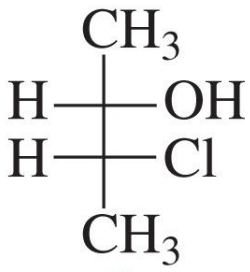


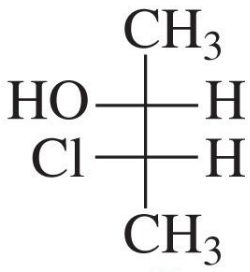


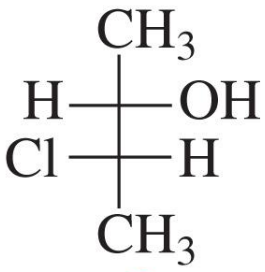


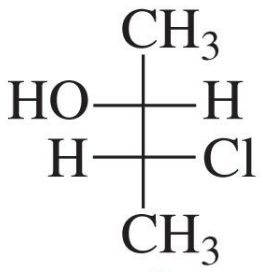
erythro enantiomers — threo enantiomers

perspective formulas of the stereoisomers of 3-chloro-2-butanol (staggered)





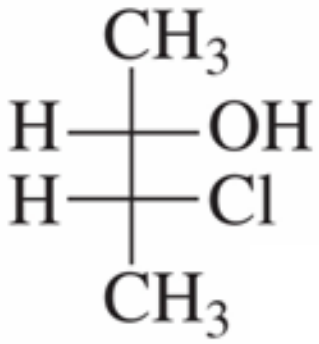




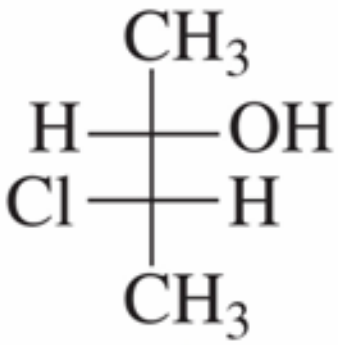
erythro enantiomers — threo enantiomers

Fisher projections of the stereoisomers of 3-chloro-2-butanol

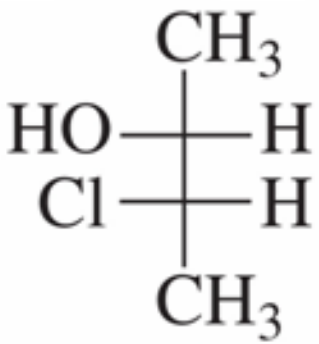
Diastereomers are stereoisomers that are not enantiomers



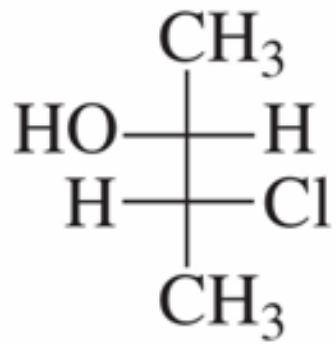
1



3

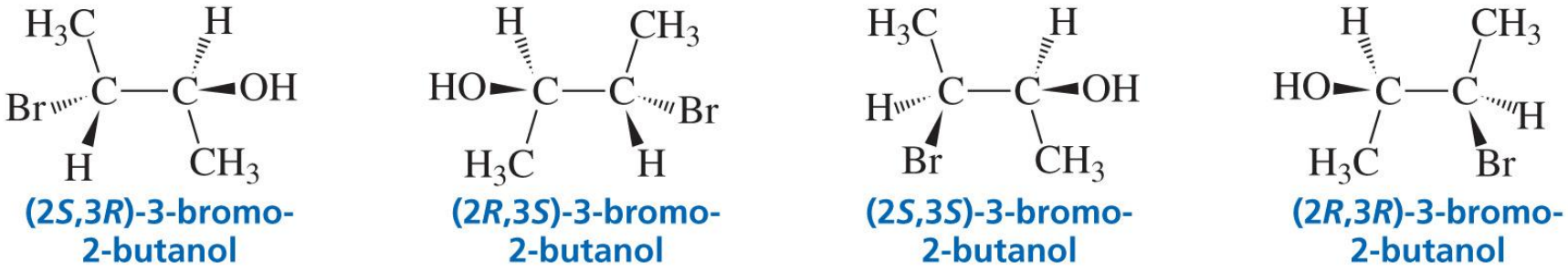


2

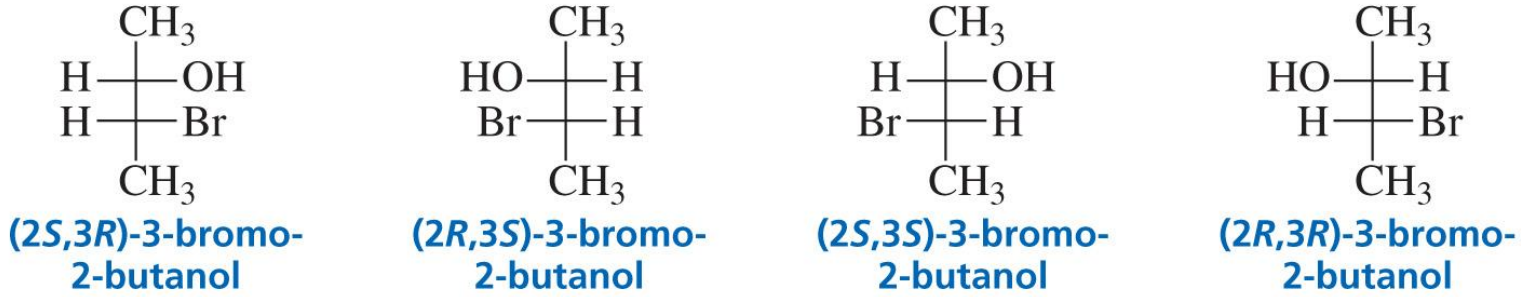


4

Diastereomers Vs Enantiomers



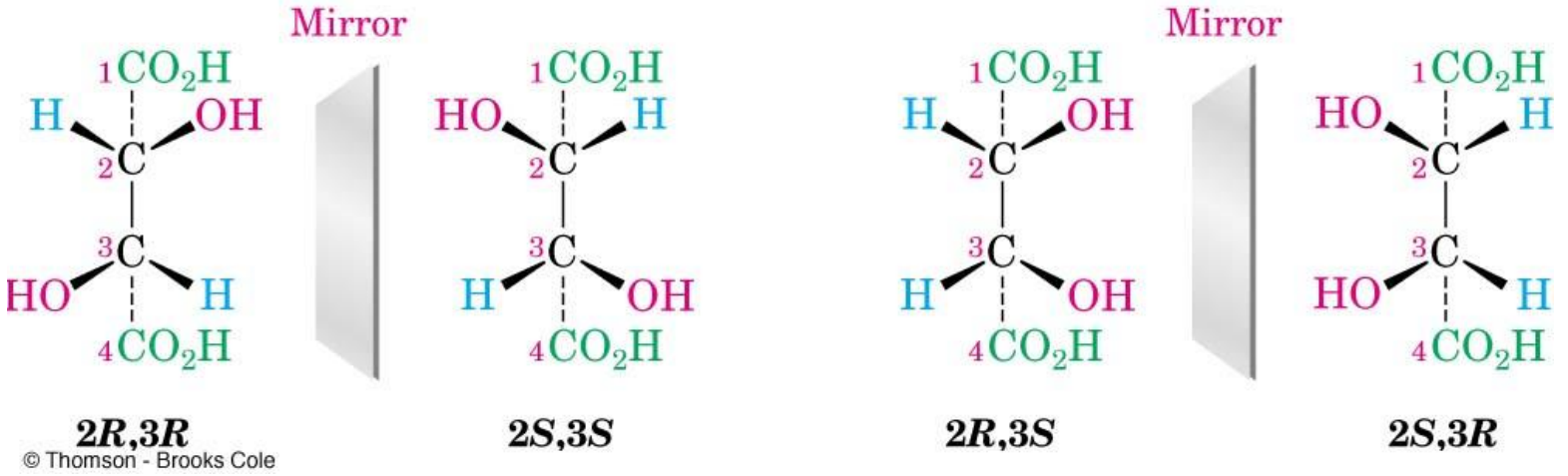
perspective formulas of the stereoisomers of 3-bromo-2-butanol

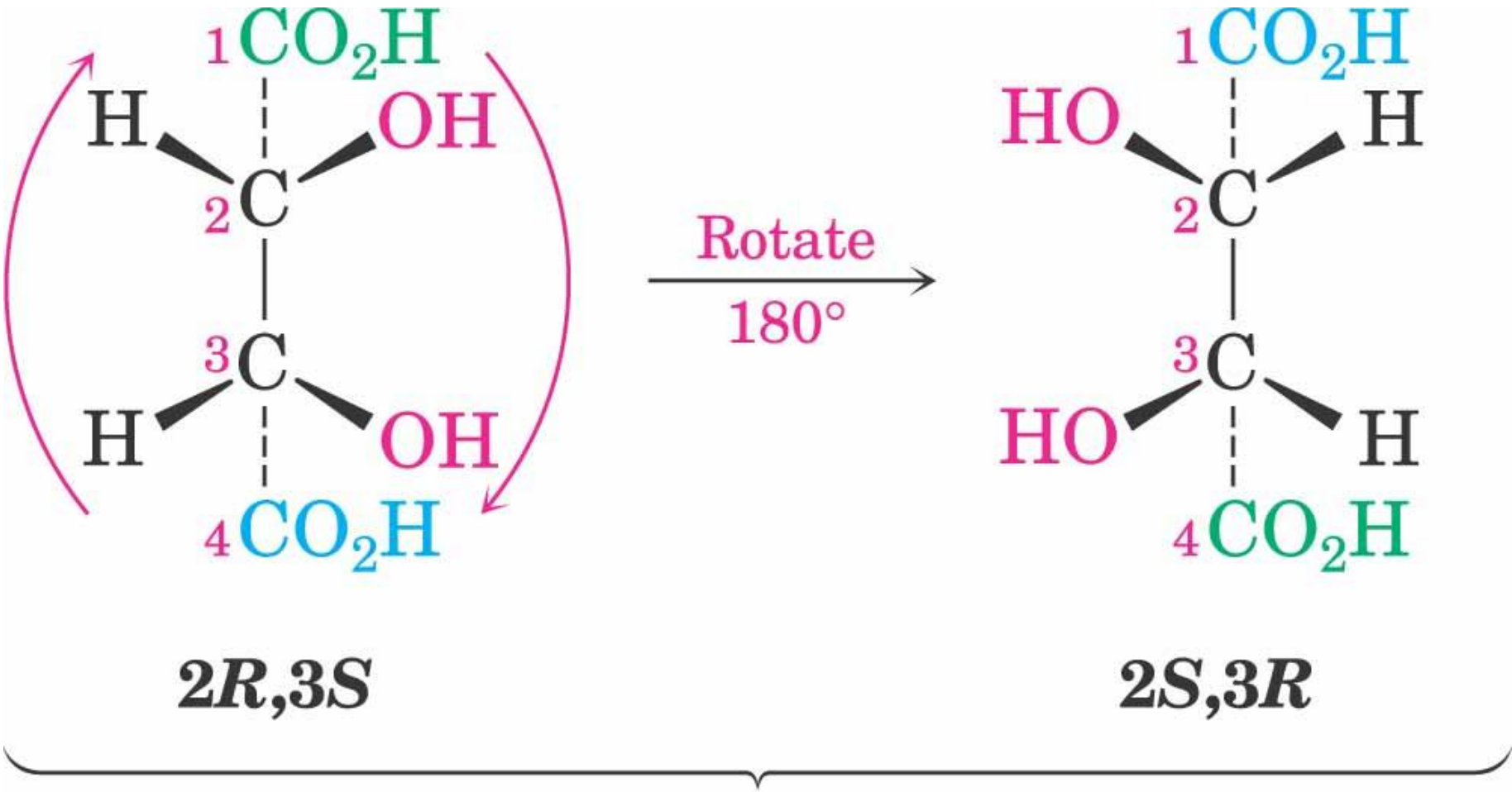


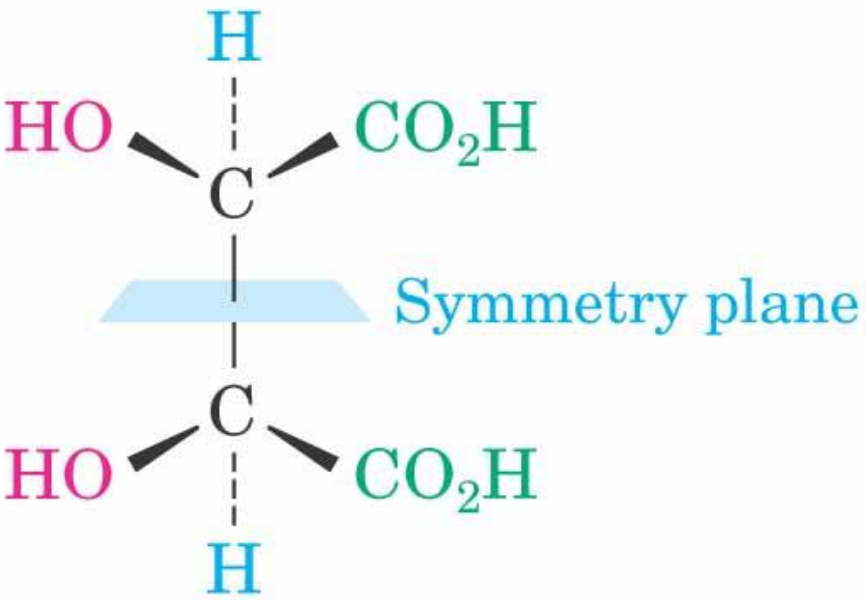
Fischer projections of the stereoisomers of 3-bromo-2-butanol

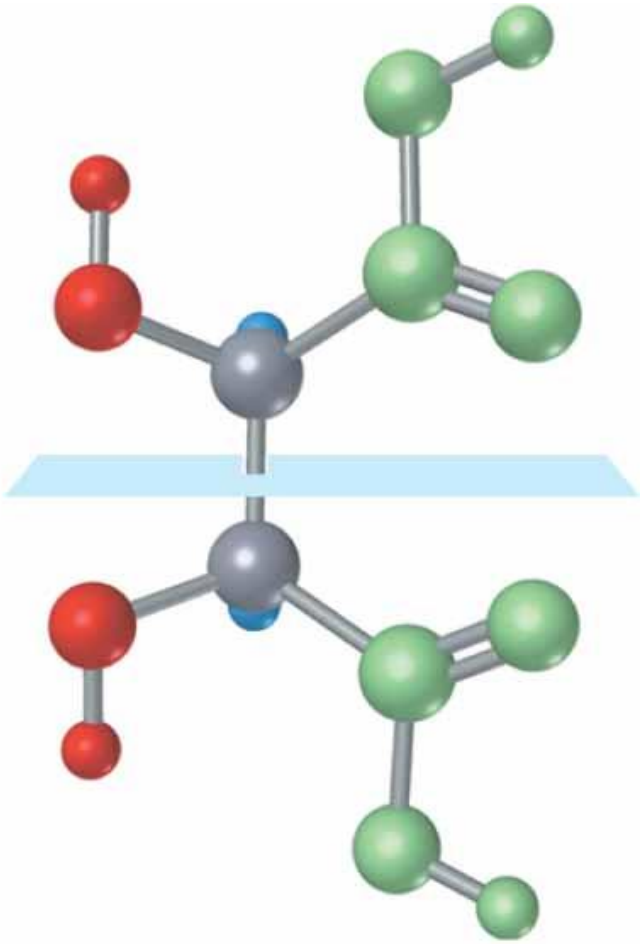
Meso Compounds

- Tartaric acid has two chirality centers and two diastereomeric forms
- One form is chiral and the other is achiral, but both have two chirality centers
- An achiral compound with chirality centers is called a *meso* compound – it has a plane of symmetry
- The two structures on the right in the figure are identical so the compound (***2R, 3S)*** is achiral





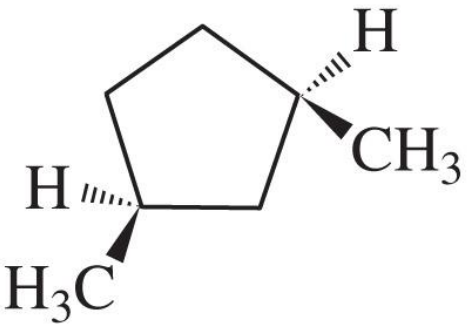




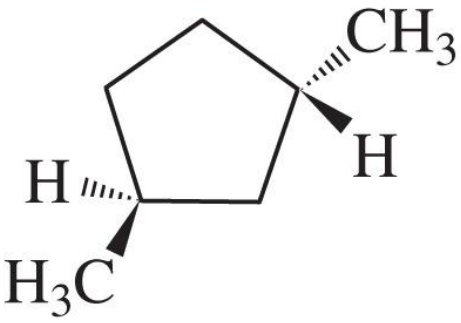
Meso Compounds optically inactive

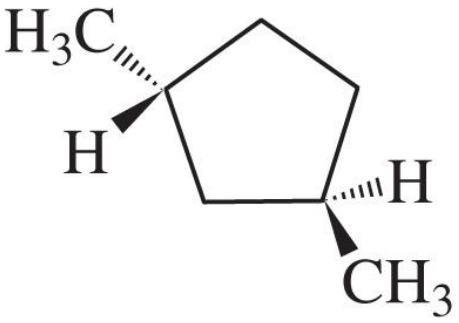
achiral molecules
Optically inactive

chiral molecules Optically active
Unless they are racemic mixture

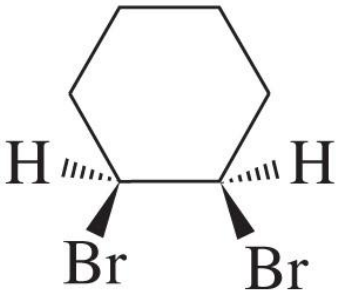


cis-1,3-dimethylcyclopentane
a meso compound

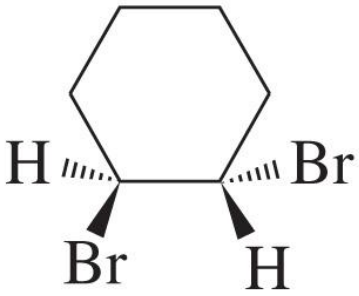


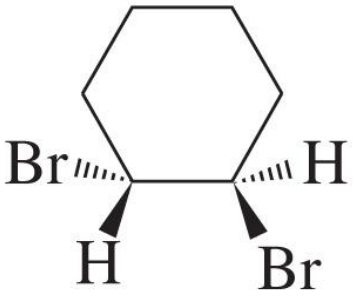


trans-1,3-dimethylcyclopentane
a pair of enantiomers



cis-1,2-dibromocyclohexane
a meso compound



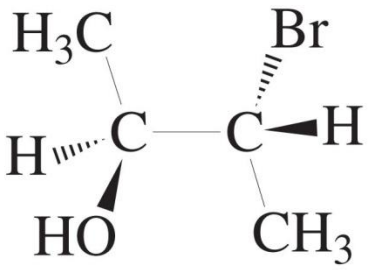


trans-1,2-dibromocyclohexane
a pair of enantiomers

Summery

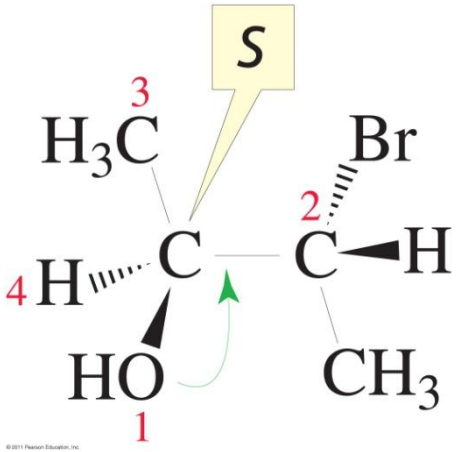
- Enantiomers have opposite configurations at each corresponding chiral carbon.
- Diastereomers have some matching, some opposite configurations.
- Meso compounds have internal mirror plane.
- Maximum number is 2^n, where n = the number of chiral carbons.

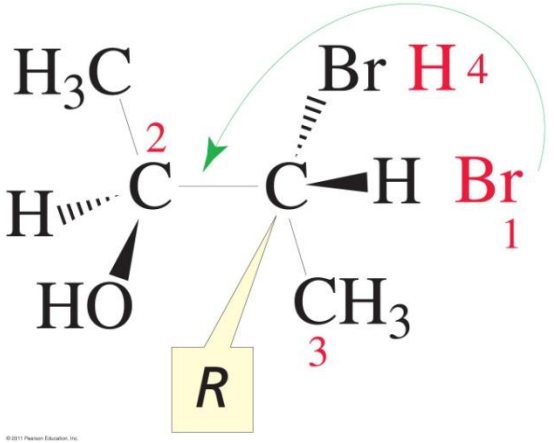
Naming Isomers with More Than One Asymmetric Center



a stereoisomer of 3-bromo-2-butanol

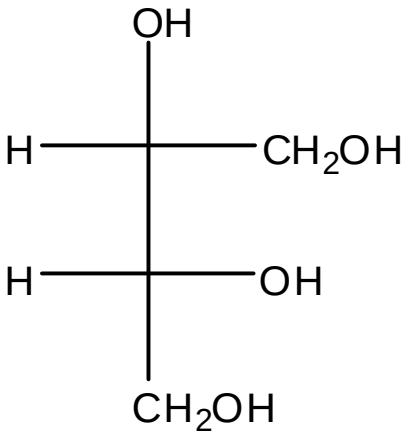
The OH group at C-2 has the highest priority, followed by Br in C-3





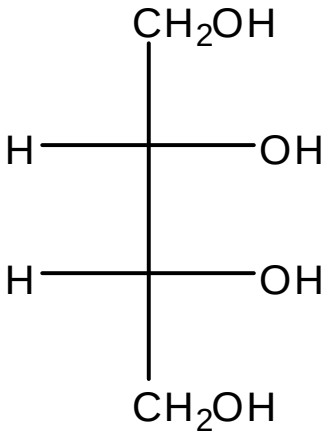
The isomer is named (2S, 3R)-3-bromo-2-butanol

Which is (are) <u>optically active.</u>
<u>Meso compounds</u>
<u>pairs of enatiomers</u>
<u>pairs of distereoisomers</u>



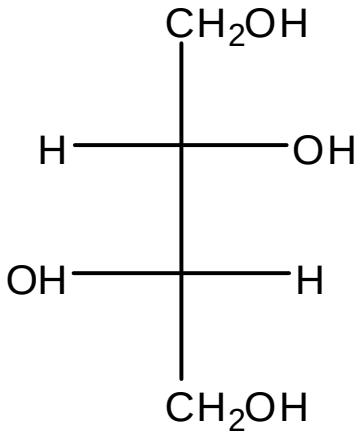
A

2R, 3R



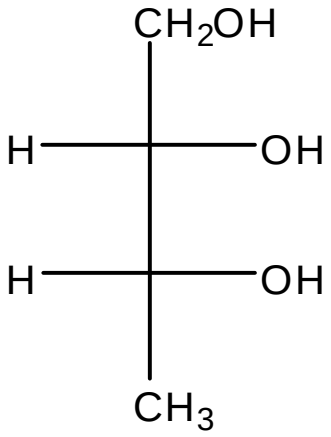
B

2S, 3R



C

2S, 3S



D